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CRYSTALLIZATION CHARACTERISTICS OF GLASS BASED ON PHOSPHORITE ORE ENRICHMENT WASTES

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It has been found that when multicomponent glass containing phosphorus oxide as an additive is subjected to low-temperature treatment ($< t_g$), crystallization accompanied by precipitation of calcium silicophosphate, not previously described in the literature, occurs in the glass powder. The compound obtained possesses cubic symmetry with space group P_p^3 and lattice parameter $a = 7.98 \text{ \AA}$.

Glasses with elevated content of iron, aluminum, and phosphorus oxides can be obtained using quartz-glaucinite wastes from the enrichment (washing and flotation) of phosphorite ore at the Egor'evskoe deposit (Moscow Oblast). Such wastes can be used to obtain decorative facing materials and technical glass ceramics with good serviceability [1–3]. At the present time phosphorites are not produced at this deposit because the reserves of rich ore have been exhausted. Kvartsit JSC is working this deposit to extract quartz sands which are used in construction and molding. Several millions of metric tons of enrichment wastes have accumulated in tailings repositories over the period the enrichment plant was active. Recently, interest in using these wastes, including in glass production, has been reappeared.

It has been shown that these wastes can be used for synthesizing glass by introducing small quantities as an admixture into the charge (soda, dolomite) [1–3]. The glass-forming melt is distinguished by elevated viscosity and rapid solidification, which makes it difficult to fabricate from such a melt articles with complex shape and precise geometric dimensions, which is especially important in the production of technical glass ceramics. The powder technology for produc-

ing glass ceramics could be promising. This method is used to produce articles by compacting finely dispersed glass powder in the presence of an organic binder followed by heat treatment during which the binder is removed and the glass crystallizes. This method makes it possible, in principle, to obtain articles with any prescribed shape. In this process, it is necessary to take account of the fact that because of the presence of iron and phosphorus oxides and the active participation of atmospheric oxygen in surface processes the glass powder can crystallize by a mechanism and with phase composition of the products that differ substantially from the crystallization of bulk glass.

We have studied the crystallization of multicomponent silicate glass containing phosphorus oxide obtained using quartz-glaucinite wastes from washing phosphorite ore at the Egor'evskoe deposit and process admixtures — soda (5%) and dolomite (15%). The chemical composition of the wastes and synthesized glass are presented in Table 1.

The glass was made in a quartz crucible placed in a flame furnace at temperature 1500°C , poured onto a steel plate, and kilned in an electric furnace. A DRON-3.0 diffractometer together with an URS-60 x-ray structural apparatus and a RKD-57.3 high-temperature x-ray debye camera (CuK_α radiation, Ni filter) were used to determine the x-ray

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TABLE 1.

Material	Mass content, %									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	K_2O	Na_2O	SO_3	calcination loss
Wastes	49.32	5.83	12.01	11.01	1.18	8.56	2.73	0.36	0.63	8.30
Glass	50.12	6.36	11.89	13.96	4.90	5.95	2.69	4.01	0.12	—

TABLE 2.

$d, \text{\AA}$	J	$d, \text{\AA}$	J
3.880	3 – 4	1.760	6 – 7
3.230	2	1.680	6 – 7
3.030	3	1.600	10
2.910	1	1.410	1
2.750	10	1.384	9
2.490	3	1.363	3
2.270	8 – 9	1.308	4
2.140	2	1.240	9 – 10
2.100	3	1.193	6
2.040	1	1.131	4
1.950	9 – 10	1.049	8 – 10

amorphousness of the glass and the phase composition of the products of crystallization.

A comparative study was made of the crystallization of bulk glass and glass powder (particle diameter $< 30 \mu\text{m}$). The samples underwent stepped heat treatment in a Silit electric furnace at temperatures from 400 to 1100°C (with holding time 30 min) in a weakly reducing medium produced by the heated rods. After extraction from the furnace the samples were cooled in air. The crystallization process was studied by investigating the phase composition of the products of heat treatment of the glass (bulk samples and powder). Together with XPA of the hardened samples, x-ray measurements were performed in the high-temperature camera.

Glass remains x-ray amorphous at temperatures below 500°C. As temperature increases, the powder starts to crystallize and 0.2 – 1.0 mm spherical inclusions begin to form. The crystalline nuclei are white and outwardly differ from the gray (at this temperature) glass powder. The main reflections of this phase ($d = 2.76, 2.27, 1.96, 1.602$, and 1.3\AA), which presumably correspond to the cubic system, appear in the x-ray diffraction pattern. The main glass powder and bulk samples remain x-ray amorphous under these conditions. The finely dispersed glass powder starts to crystallize at temperatures below the glass formation temperature ($t_g \sim 580^\circ\text{C}$) as result of solid-phase reactions.

As temperature increases, the size and compaction of the spherical inclusions decrease. The main glass powder acquires a brown color, probably because of surface oxidation of Fe^{2+} . X-ray diffraction shows that magnetite FeFe_2O_4 precipitates at temperatures above 630°C in the powder and at 660°C in the bulk glass. Tetracalcium phosphate $4\text{CaO} \cdot \text{P}_2\text{O}_5$ separates in the bulk glass together with magnetite, and for $t_g > 700^\circ\text{C}$ monoclinic pyroxene, identified as augite, becomes the predominant crystalline phase. The glass powder and the surface of the bulk samples acquire a red-brown color because of the formation of hematite $\alpha\text{-Fe}_2\text{O}_3$ on the surface.

TABLE 3.

$d, \text{\AA}$	J	Symmetry of a unit cell with $a = 7.84 \text{\AA}$
2.750	10	220
2.770	8 – 9	004
1.950	9 – 10	400
1.600	10	422
1.240	9 – 10	620
1.049	8 – 10	642

The parameters of the reflections of the high-precision powder diagrams of white spherical inclusions taken from a sample hardened at 500°C are presented in Table 2. This phase could not be identified according to the ASTM card catalog and x-ray indices [4, 5]. The extent to which this compound can be identified on the basis of x-ray measurements and calculations performed on the basis of such measurements is not described in the literature. X-ray fluorescence analysis (VRA-30R spectrometer) points to a composition close to the salt CaP_2SiO_8 .

Direct indexing according to the interplanar distances gave the parameter $a = 3.92 \text{\AA}$ for the substance being studied. This value is impossible according to crystal-chemical considerations, so that the initial value was doubled to determine the space group more accurately and to obtain the final indexing. The computed indices of the main phases of the calcium silicophosphate synthesized are presented in Table 3.

The compound obtained is a calcium silicophosphate, it possesses cubic symmetry with $a = 7.84 \text{\AA}$, and its space group is P_p^3 . Thus, as result of solid-phase reactions, synthesis of calcium silicophosphate with a primitive structure deformed along the L_3 axis is possible at temperatures below the glass formation temperature.

The effect determined here must be taken into account when working out a devitrification regime for iron-containing glasses which also contain phosphorus oxide. We note that in our opinion phosphorus oxide is not a direct nucleator for the crystallization of this glass. As result of its crystal-chemical characteristics, phosphorus forms liquation micro-nonuniformities in matrix silicate glass, which easily crystallize in the glass powder, forming thermally unstable calcium silicophosphate.

Magnetite FeFe_2O_4 microcrystals, which first precipitate on the interfaces between the phases, can act as crystallization nucleators. Volume crystallization proceeds with the formation of tetracalcium phosphate $4\text{CaO} \cdot \text{P}_2\text{O}_5$ and monoclinic pyroxene of the augite type together with active surface oxidation of divalent iron and conversion of magnetite into hematite $\alpha\text{-Fe}_2\text{O}_3$. Decorative iridescent films are observed on bulk glass samples; glass powder acquires a distinct brown color characteristic for hematite.

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